Anharmonic Vibrational Properties from Intrinsic n-Mode State Densities

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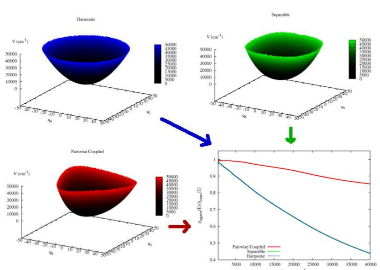
Abstract

A method for calculating fully anharmonic vibrational state counts, state densities, and partition functions for molecules is presented. The method makes use of a new quantity, the *intrinsic* density of states, which is associated with the states that uniquely arise from a given mode, mode pairing, or higher-order mode coupling. By using only low-order intrinsic densities, the fully-coupled anharmonic vibrational result can be constructed, as shown by our application of the method to methane, CH_4, and cyclopropene C_3H_4. Truncation of the intrinsic expansion at the coupling of pairs of modes yields greatly improved scaling over direct evaluation of the full-dimensional result and recovers a large fraction of the total anharmonicity. We also discuss the relation of the new quantities to the structure of the potential energy surface.



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Accurate predictions of kinetics and thermodynamics depend critically on accurate evaluation of the rovibrational density of states, $\rho(E)$, and its related quantities.[1–4] In the classic Rice, Ramsperger, Kassel, and Marcus (RRKM) theory of unimolecular reactions, the rate constant is proportional to the number of states at the transition state divided by the density of states of the reactant. Similarly, in bimolecular canonical transition state theory (TST) the rate constant is dependent on the density of states through the appearance of partition functions corresponding to the reactants and to the transition state.[2] Unfortunately these quantities are difficult to evaluate accurately for several reasons, including: the need for proper quantization, couplings between rotations and vibrations, and anharmonic couplings amongst the vibrations. In this letter we present a general and efficient scheme for including the important anharmonic coupling.

A common approximation, which makes the computation of $\rho(E)$ quite amenable, is to use a separable model in which every vibrational degree of freedom is assumed to be totally uncoupled from any of the others. Most often each mode is further assumed to be harmonic, although sometimes modes are given special treatment as Morse oscillators, hindered rotors, etc... Algorithms and computer implementations of these methods, e.g., the semiclassical Whitten-Rabinovitch (WR) approximation,[5] the Beyer-Swinehart (BS)[6] and Stein-Rabinovitch (SR)[7] state counting algorithms, or the steepest-descent method,[4] are readily available. As might be expected, at higher energies these approximations can significantly underestimate the anharmonicity because of the neglect of the coupling between vibrational modes. This is true even when the underlying independent vibrations are treated as anharmonic oscillators.[8,9]

Many attempts have been made to improve on the separable approximation by looking at the specific coupling between different modes. For instance, the coupling of bends to stretches has been studied and empirical models describing this coupling have been constructed,[10–13] the role of stretch-stretch coupling was been investigated in triatomic systems,[12,14] numerous methods for treating torsional motions have been developed,[2,3,15–18] and Monte-Carlo integration has been applied to calculation of quantum vibrational states using a spectroscopic (e.g., Dunham[19]) expansion which includes some anharmonic terms.[20–23] It is also worth noting the recent semi-empirical work of Schmatz[24] as well as the thermodynamic method, which relies on experimental data,[25,26] the density correlation function method of Jeffreys *et al*,[27,28] and the use of path-integral methods to calculate the quantum partition function directly.[29,30] The accurate inclusion of the coupling terms, however, remains an open issue.

Despite its associated problems, separability has certain nice features which we wish to retain. It allows a complex problem, the calculation of the full-dimensional coupled density of states, $\rho(E)$, to be broken down into a set of small, readily computable quantities that can be then reassembled to yield the full result. As such it renders large, potentially intractable problems amenable to computation. In this letter we propose a method for the efficient construction of the anharmonic density of states via an expansion in terms of *intrinsic* n-mode densities of states. This formalism includes the separable approximation at its lowest order and is systematically improvable by including the effect of coupled pairs, triples, etc... of modes. Furthermore, we show that, while accurate results are not obtained with 1-mode intrinsics, accurate results can be obtained via 2-mode intrinsic state densities.

The intrinsic n-mode densities of states correspond to the component of the density of states that cannot be generated by convolutions of lower-mode densities of states and will be denoted, Δ. The *intrinsic* two-mode density of states,

$$\Delta_{ij}(E) = \rho_{ij}(E) - \rho_i(E) * \rho_j(E), \tag{1}$$

where $\rho_{ij}(E)$ is the exact density of states spanned by modes i and j while $\rho_i(E)$ and $\rho_j(E)$ are the one-mode densities of states associated with each individual mode and the notation $a * b$ denotes the convolution. Here the one-, two-, and reduced-mode densities are calculated with the remaining coordinates fixed at some reference. The intrinsic three-mode density of states is, similarly,

$$\Delta_{ijk}(E) = \rho_{ijk}(E) - \rho_i(E) * \rho_j(E) * \rho_k(E) - \Delta_{ij}(E) * \rho_k(E) - \Delta_{ik} * \rho_j - \Delta_{jk}(E) * \rho_i(E). \tag{2}$$

Comparisons of the 2- and 3-mode intrinsic state densities with full 2- and 3-mode state densities are shown in Fig. 1.

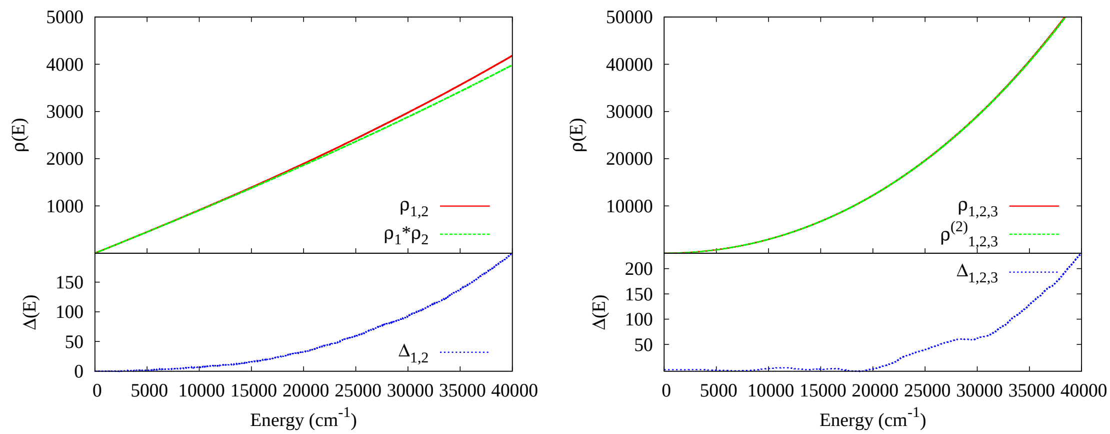

Figure 1: Selected 2- and 3-mode intrinsic densities of states for the indicated mode combinations of CH_4.

The practical usefulness of the previous equations is that one can make general expressions for the full dimensional molecular state density through various orders of the n-mode intrinsic state density. At first order the method reduces to the usual separable approximation. At second order, $\Delta_{ijk}(E)$ and all higher-order intrinsics are set to 0 and one can write the following equations for the pairwise coupled 3- and 4-mode systems:

$$
\begin{aligned}
\rho^{(2)}_{ijk}(E) &= \rho_i(E)*\rho_j(E)*\rho_k(E)+\Delta_{ij}(E)*\rho_k(E)+\Delta_{ik}(E)*\rho_j+\Delta_{jk}(E)*\rho_i(E), && (3)\\
\rho^{(2)}_{ijkl}(E) &= \rho_i(E)*\rho_j(E)*\rho_k(E)*\rho_l(E)+\Delta_{ij}(E)*\rho_k(E)*\rho_l(E)\\
&\quad +\Delta_{ik}(E)*\rho_j(E)*\rho_l(E)+\Delta_{jk}(E)*\rho_i(E)*\rho_l(E)+\Delta_{il}(E)*\rho_j(E)*\rho_k(E)\\
&\quad +\Delta_{jl}(E)*\rho_i(E)*\rho_k(E)+\Delta_{kl}(E)*\rho_i(E)*\rho_j(E)+\Delta_{ij}(E)*\Delta_{kl}(E)\\
&\quad +\Delta_{ik}(E)*\Delta_{jl}(E)+\Delta_{il}(E)*\Delta_{jk}(E), && (4)
\end{aligned}
$$

where the superscript (n) indicates the order of the approximation. Generalization to larger molecular systems and/or to higher n-mode approximations is straightforward. While the previous equations are suitable to continuous ρ, i.e., those derived from classical expressions, with slight modification they can be used for discrete, i.e., quantum, ρ. For discrete states, the pairwise coupled

3-mode system is

$$\rho_{ijk}^{(2)}(E) = \rho_i(E) * \rho_j(E) * \rho_k(E) + \frac{1}{3}\Delta_{ij}(E) * \rho_k(E) + \frac{1}{3}\Delta_{ik}(E) * \rho_j + \frac{1}{3}\Delta_{jk}(E) * \rho_i(E), \qquad (5)$$

where the extra factors of $\frac{1}{3}$ arise from the requirement that $\rho_{ijk}^{(2)}(E) \geq 0$.

Here, we have applied the 2-mode version of method to the calculation of state counts, densities of states, and partition functions for methane, CH_4, and cyclopropene, C_3H_4. Classical phase space integrals for state counts and densities of states were evaluated using our recently published Monte Carlo algorithm, MCPSI.[31] For methane, we also demonstrate the quantized version of the method where we solve for the ρ_i and Δ_{ij} using 1- and 2-dimensional vibrational Hamiltonians and compare with full-dimensional vibrational configuration interaction (VCI) results. In all cases, the coordinates employed are mass-weighted Cartesian normal modes and calculations correspond to the vibrational states with zero angular momentum.

As a test of the 2-mode coupling scheme we have used methane with a tight-binding potential.[32,33] This potential is a good approximation to the true *ab initio* potential and has the advantage of being exceptionally quick to evaluate. With this potential we can easily achieve millions of samples for all of the Monte Carlo runs and this tightly converge the results and minimize any effects of statistical noise. For reference, the vibrational frequencies of CH_4 with this potential are $\nu_1 = \nu_2 = \nu_3 = 1573$ cm^{-1}, $\nu_4 = \nu_5 = 1692$ cm^{-1}, $\nu_6 = 3157$ cm^{-1}, and $\nu_7 = \nu_8 = \nu_9 = 3248$ cm^{-1}, where we have reflected degeneracies by repeating frequencies in the list so that the subscripts also number the 9 normal modes. The accuracy of the pairwise coupled densities of states is shown in Fig. 2 where it is compared with the separable approximation and with the fully coupled result. The agreement of $\rho^{(2)}$ with the full-mode coupled density of states is excellent for the classical densities, whereas the usual separable approximation under-predicts the state density by a factor of 2 at threshold. For this system, $\rho^{(1)}$ results in negligible improvements over the harmonic case due to cancellation of positive and negative anharmonicities. The comparison of the integrated quantum density of states, W, is also shown in Fig. 2. While the pairwise coupled approximation yields a general shift of states to lower energies, it is only a small improvement over the separable case. It is worth noting, however, that applying a classically calculated anharmonicity correction to the quantum harmonic vibrational properties may yield good agreement with results based on direct state counts.[31]

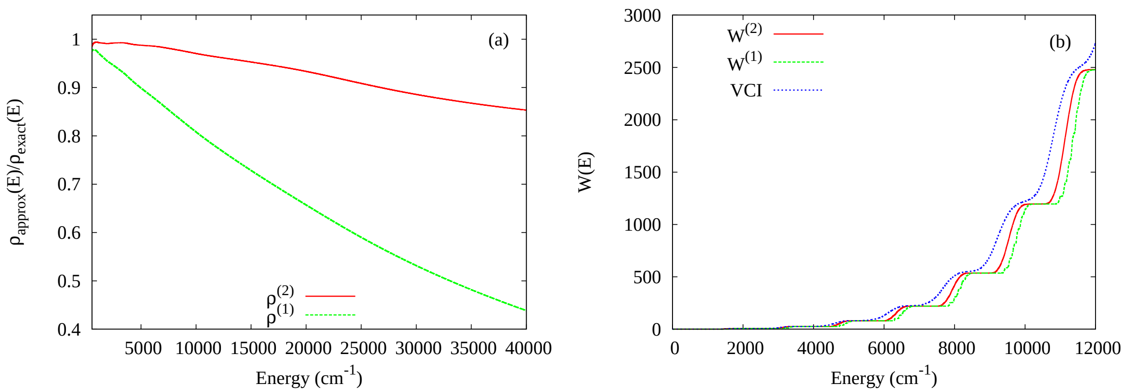

Figure 2: Accuracy of separable and pairwise coupled approximations to (a) the classical density of states and (b) the integrated quantum density of states for methane.

One might assume that only certain modes (i.e., those that are similar in frequency or in other criteria) couple, and we can test this hypothesis by looking at the 2-mode intrinsic densities. Within the normal coordinate representation used here, almost all of the modes couple with all of the other modes. In particular, most of the low-frequency bends couple to the high-frequency stretches, and it is the anharmonicity from this intermode coupling that yields a large portion of the total anharmonicity of the full result as shown in the Supporting Information (SI). When using normal modes, at least, this result underscores the necessity of including the coupling between all pairs of normal modes in order to recover the full anharmonicity.

We have also tested the accuracy of the pairwise coupled state densities for cyclopropene, for which we employed a direct *ab initio* potential at the B3LYP/6-311++G(d,p) level of theory. All electronic structure calculations employed the Gaussian 09 package.[34] Results are compared with a calculation of the full-dimensional density of states in Fig. 3. Evaluation of the pairwise coupled density of states is significantly less computationally demanding. While adequately converging the full-mode density of states for cyclopropene took approximately 125,000 hours of computer time, the equivalent calculation of the two-mode coupled state density required only 4,000 computer hours using the same cluster. The accuracy of $\rho^{(2)}$ is very good for cyclopropene and it is a signif-

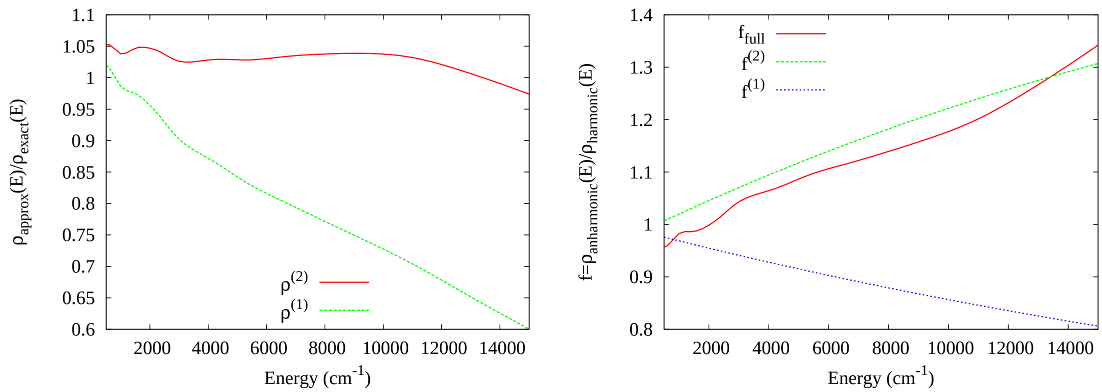

Figure 3: Accuracy of the separable (1-mode) and pairwise (2-mode) densities of states for cyclopropene.

icant improvement over $\rho^{(1)}$. Due to several of the modes having large positive anharmonicities in cyclcopropene, the harmonic approximation yields better results than the separable approximation.

To further motivate the intrinsic n-mode densities, it is useful to consider their relation to potential energy surfaces. The potential energy of a molecule with n degrees of freedom may be expanded about a specific geometry as

$$V_{\text{Taylor}}(q_1,\ldots,q_n) = V_0 + \sum_i \frac{\partial V}{\partial q_i} q_i + \sum_{i,j} \frac{1}{2} \frac{\partial^2 V}{\partial q_i \partial q_j} q_i q_j + \ldots, \tag{6}$$

where V_0 is the potential energy at the reference geometry and q_i are the coordinates which we take without loss of generality to be 0 at the reference structure. The expansion given in Eq. 6 corresponds to the standard multivariable generalization of the Taylor series, and the polynomial order of the expansion defines both the maximum number of degrees of freedom that can be coupled as well as the maximum order of the coupling. Alternatively, we can expand the potential as

$$V_{n-\text{MR}}(q_1,\ldots,q_n) = V_0 + \sum_i V^{(1)}(q_i) + \sum_{i<j} V^{(2)}(q_i,q_j) + \ldots, \tag{7}$$

where

$$
\begin{aligned}
V^{(1)}(q_i) &= V(q) - V_0 \,|\, q_n = 0 \forall n \neq i \\
V^{(2)}(q_i, q_j) &= V(q) - V^{(1)}(q_i) - V^{(1)}(q_j) - V_0 \,|\, q_n = 0 \forall n \neq i, j\,.
\end{aligned}
\tag{8}
$$

The arrangement of the sum in form given by Eq. 7 and Eq. 8 is usually termed the *n*-mode representation (nMR), and has a been used extensively in the vibrational dynamics community.[35] For convenience in the subsequent equations, we will drop the zeroth-order term V_0 since this can always be removed by an appropriate shift of the energy. Different approximations to ρ involve the truncation of either Eq. 6 or Eq. 7 at different orders. For instance, direct state counts based on a perturbation theory expansion of the vibrational energy levels, for instance the methods based on the Dunham expansion, often involve the truncation of Eq. 6 at the quartic level. The equations proposed here, however, truncate Eq. 7 at a specified number of modes rather than an order of polynomial expansion and coupling to infinite order within each pair, triple, etc... is included.

We will now explicitly consider the form of the two-mode intrinsic density of states. For two modes, the number of states with energy less than or equal to E is given by,

$$
W_{ij}(E) \equiv \int_0^E \rho_{ij}(x)dx = \frac{2\pi}{h^2}\int \Theta[E-V]\,\left(E - V(q_i, q_j)\right) dq_i dq_j, \tag{9}
$$

where h is Planck's constant, Θ is the Heaviside step function, and we have already performed the analytic integration over the momenta. For a more detailed explanation of this procedure, we refer the reader to the details of our Monte-Carlo algorithm.[31] Substituting the expression for the pairwise coupled state densities into Eq. 9 yields,

$$
W_{ij}(E) = \frac{2\pi}{h^2}\int \Theta[E-V]\,\left(E - V^{(2)}(q_i, q_j) - V^{(1)}(q_i) - V^{(1)}(q_j)\right) dq_i dq_j\,. \tag{10}
$$

Now introducing the the separable approximation for the potential we arrive at, after some manipulation,

$$\begin{aligned}
W_{ij}(E) &= \frac{2\pi}{h^2}\int \Theta[E-V^{(1)}]\,(E-V^{(1)}(q_i)-V^{(1)}(q_j))\,dq_i\,dq_j \\
&-\frac{2\pi}{h^2}\int \Theta[E-V^{(1)}]\,V^{(2)}(q_i,q_j)\,dq_i\,dq_j \\
&+\frac{2\pi}{h^2}\int (\Theta[E-V]-\Theta[E-V^{(1)}])\,(E-V_2(q_i,q_j)-V^{(1)}(q_i)-V^{(1)}(q_j))\,dq_i\,dq_j
\end{aligned} \tag{11}$$

where we have used $V^{(1)} = V^{(1)}(q_i) + V^{(1)}(q_j)$. The first term is the state count obtained via the 1-mode separable approximation. The second term of Eq. 11 corresponds to a correction over the region defined by $\Theta[E-V^{(1)}]$ due to the potential coupling $V^{(2)}$. When the sign of $V^{(2)}$ is negative, meaning that the sum of $V^{(1)}$ terms yields too high of an energy, the number of states is increased, whereas when the sign of $V^{(2)}$ is positive the number of states is decreased. An example of $V^{(2)}$ is shown in the SI for methane. The final piece of Eq. 11 corresponds to a correction due to the expansion or contraction of the integration region because of $V^{(2)}$. An example of this correction is shown in Fig. 4 for a stretch-bend coupling (q_2, q_8) and a stretch-stretch coupling (q_7, q_8) for methane. From the plots in Fig. 4 and the SI it is apparent that both pieces of the correction could be important; however, from the specific examples we have looked at in both methane and cyclopropene, the third term of Eq. 11 has been the more important. From the associated plot, one can also see some of the fortuitous cancellation of errors that occurs in the harmonic approximation. Whereas the sum of the one-mode terms leads to a compression of the integration region compared to its harmonic approximation at each specified energy, the full potential both compresses the region along certain axes and expands it along others.

We have introduced a mode coupling scheme based on hierarchical n-mode expansions and have demonstrated that accurate full-dimensional anharmonic state densities may be obtained by truncating the representation at 2nd order, i.e., by considering only a pairwise coupled representation. As shown for methane and cyclopropene, the pairwise coupled method yields a significant improvement in the calculated density of states over either the harmonic approximation or the one-dimensional, separable approximation. In addition, the method we have developed can be sys-

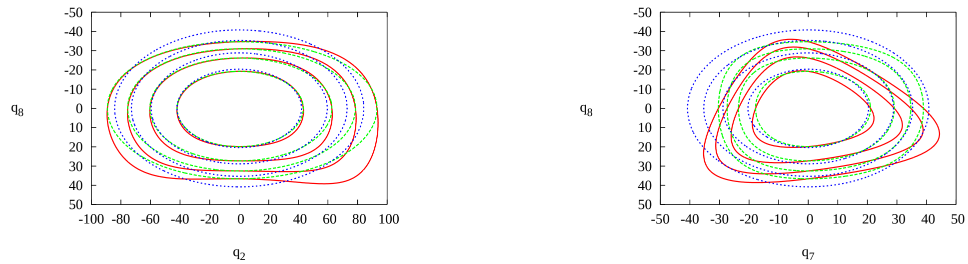

Figure 4: Contour plots of $V(q_2,q_8)$ and $V(q_7,q_8)$, in red, versus $V^{(1)}(q_2)+V^{(1)}(q_8)$ and $V^{(1)}(q_7)+V^{(1)}(q_8)$, in green, and the respective harmonic approximations, in blue for CH_4. Contour lines are at 10 000, 20 000, 30 000, and 40 000 cm^{-1} respectively.

tematically improved by the inclusion of important 3- or higher-mode couplings. While the use of normal modes uncouples them at second order for infinitesimal displacements, they may not be the most efficient coordinates for vibrational calculations in general. We and other authors have discussed alternative coordinate choices with which to perform vibrational calculations,[31,36–40] and the present approach can benefit from these efficiency improvements as well. For instance, one could attempt to minimize $\Delta_{ijk}(E)$ with respect to the coordinates. Here we have evaluated the classical intrinsic n-mode density using MCPSI, and also shown that it is possible to apply this correction by using quantum mechanically calculated $\Delta_{ij}(E)$. This method offers an approach to intermode coupling through the use of functions that are dependent on two or more modes, which may be of use in the calculation of kinetic and thermodynamic quantities.

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Supporting Information Available

Plots of the two-mode intrinsics showing bend-bend, bend-stretch, and stretch-stretch couplings in CH_4 and a sample plot of $V^{(2)}$ for one pair of modes. This material is available free of charge via the Internet at http://pubs.acs.org

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